

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Concerning Organometallic Compounds in Environment: Occurrence, Fate, and Impact

Kovacs Melinda Haydee and Kovacs Eموke Dalma

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/67755>

Abstract

Organometallic compounds can be found in our surrounding environmental compartments either because of human extensive activities or their existence as natural products in the environment. Since organometallic species of trace metals were found often more worrying than their parent compounds, intensive research on their properties, pathways of transformation in different environmental compartment as well as their fate and interactions between different environmental compartments (under different external and internal conditions), and not finally their end-up and disposal, has become a requirement from many public health and environmental protection agencies.

Keywords: organomercury, organotin, organolead, environment

1. Introduction

In environment, most of organometallic compounds were found as persistent that do not easily decompose but are easily concentrated and are highly toxic, often more toxic than their elemental form Refs. [1, 2]. These compounds could be characterized as they have a metal or metalloid-carbon bond. Usually the bonds in them are covalent and are reached between soft acid metals and soft ligands. In environment, their fate and pathways occur through interactions with other chemicals and biota from the environmental compartment, their cycling and pathways between multiple environmental compartments and phases are physically, chemically, and biologically mediated [3].

Concerns considering organometallic compounds are accentuated also by that once they accumulate in different environmental compartments can inhibit their functioning and consequently

affect the ecosystem, plants, and other living organisms (micro and macro), and also contaminate the food chain (including that of humans) [4–6].

As natural components of the Earth's crust and resultant of biogeochemical reactions, organometallic compounds are generally present at low concentrations in natural environmental compartments, as soil or water, but extensive anthropogenic activities over the past 50 years (industrial, mining, agricultural, and urban-extension activities) have greatly increased their inputs in different compartments of our surrounding environment; thus, their presence is becoming a severe problem at worldwide level [7–10].

Among all compartments, soil plays an important role in the distribution and fate of organometallic compounds, since often it serves as a major reservoir and sink of these pollutants due to its large absorption capacity [11, 12]. In the terrestrial and aquatic environment, metals occur in both organic and inorganic forms, including elemental forms, salts, and organometallic compounds. In most cases, the mineral form of metals is insoluble thus rendering these species rather unavailable for transport or plant uptake in the short term [5].

Inorganic species are adsorbed onto soil organic matter and/or metal oxides which can be subjected to biogeochemical processes (e.g., reduction, oxidation, methylation, alkylation, and biomethylation) resulting in highly mobile organic species that further have the ability to form water-soluble complexes in living organism body tissues thus increasing the potential for uptake and accumulation by organisms [13, 14]. Moreover, bond formation between methyl, ethyl, or alkyl groups and metals or metalloids cause changes in their physical properties as solubility or volatility, properties that could significantly affix their fate, pathways, and life cycle both in the original environmental compartment and between interconnected environmental compartments. The rates of all these processes depend greatly on the local conditions, which exist in the relevant ecosystem and the microbial activity, as the pollutant's leaching rate strongly depends on its specific geochemical properties [15, 16].

2. Concerning organometallic compounds occurrence in environment from anthropogenic sources

The compounds considered in this work are those having environmental implications and are susceptible to threat biota and human health. Thus, we limited this chapter to organic forms of mercury, lead, and tin. These compounds could occur in environment either naturally or deposited as an industrial pollutant.

2.1. Mercury and its organic derivatives

Mercury (Hg) is a nonessential and extremely toxic trace element that poses global environmental and human health risks [5, 13]. Its biogeochemical cycle was perturbed during the last centuries by anthropogenic inputs. The organic forms of mercury compounds have been used in chlor-alkali plants and coal power station industry, and also in other anthropogenic activities, such as catalysts, fungicides, herbicides, disinfectants, and pigments [5, 12, 13]. Emissions

and inputs from those mentioned industrial processes as well as from the combustion of fossil fuels and waste disposal finally resulted in severe environmental contamination [17, 18].

As mentioned in many studies, mercury and its related compounds are considered health hazards, but their toxicity depends strongly on their chemical forms, those organic forms of mercury, such as methylmercury or dialkyl mercury, are considered more toxic than inorganic salts of mercury [19, 20].

- (1) Generally, metal speciation marks both the fate as well as the toxicity of metals in environmental compartments, that speciation adverts to the occurrence of the different variety of chemical forms of a specific metal in the environment. Such forms of metals could be free ions, complexes (dissolved in solution or sorbed on solid surfaces) or as forms that have been coprecipitated in major metal solids or which occur in their own solids [3]. Considering scientific reports regarding mercury species toxicological effects, it becomes necessary to speciate mercury [21]. Lindqvist et al. [22] categorized the mercury species compounds into three categories: (i) volatile species (Hg); (ii) reactive species (Hg^{2+} , HgO on aerosol particles, Hg^{2+} complexes with OH , Cl , Br , and organic acids); and (iii) non-reactive species (CH_3Hg^+ and other organomercurial moieties, $\text{Hg}(\text{CN})_2$, HgS and Hg^{2+} bond to sulfur in fragments of humic matter) [20]. The speciation of mercury and its related compounds affects, besides the degree of toxicity, also its properties (e.g., volatilization, photolysis, sorption, atmospheric deposition, acid/base equilibrium, diffusivity, microbial transformation degree, and pattern) that characterize their fate and pathways in the environment [3]. The organic species of mercury that were found to be important from hazard and toxicological point of view and those are prevalent in environment are as follows: methylmercury (CH_3Hg^+), ethylmercury ($\text{C}_2\text{H}_5\text{Hg}^+$) [23, 24], phenylmercury ($\text{C}_6\text{H}_5\text{Hg}^+$) [25], and dimethylmercury ($(\text{CH}_3)_2\text{Hg}$) [26].

2.2. Lead and its organic derivatives

Inorganic lead is introduced into the natural environment from several sources, but organolead compounds are mainly exhausted into the air from the petroleum industry and automobiles, and then they contaminate soil and water sources [27].

Lead organic forms, such as tetramethyl lead and tetraethyl lead have been widely used as anti-knocking agents in fuels. Although in the past decade lead gasoline consumption decreased considerably, there are still countries around the globe that use it [28, 29]. Currently, gasoline used in aviation remained the fuel with the highest alkyl lead content, in those days sources of alkyl lead in surrounding environment are airport fuel terminals, bulk aviation, gasoline plants, bulk leaded racing, and other nonroad vehicles gasoline plants, spills from fuel loading, transfer storage, and fuelling [27].

Alkyl lead compounds, such as tetra-alkyl lead are easily absorbed by living organisms due to their lipophilic character. Their absorption depends on the nature of the compound, exposure time, and nature of organism [27, 30]. Toxicological studies on human beings have been demonstrated that cumulative chronic exposure to organic forms of lead is more toxic than

those to inorganic forms of lead [31]. According to Gallert and Winter [30] and Pyrzynska [32], the toxicity of alkyl lead compounds decreases with a decreasing number of ethyl or methyl moieties or with a decreasing number of carbon atoms (ethyl lead \rightarrow methyl lead) according to the following sequence: $R_4Pb > R_3Pb^+ > R_2Pb^{2+}$, with R being either $-CH_3$ or $-C_2H_5$ [27].

2.3. Tin and its organic derivatives

Organotin compounds are organometallic compounds in which carbons are bonded directly to tin (R_nSnX_{4-n} , where n is between 1 and 4, and R is an alkyl or aryl group) [33]. Organometallic forms of tin have been used as active agents in a wide range of applications in industry, such as stabilizers in the polyvinyl chloride industry, plastic additives production, industrial catalysts, antifouling paints, wood preservatives, and in agriculture as biocide products (insecticides, fungicides, and bactericides) [33–35].

Nowadays, use of organotin compounds as anti-foulant has been banned due to their severe toxic effects on the aquatic organisms [36]. Moreover, use of tributyl tin and triphenyl tin compounds in various industrial applications has raised a great concern in the last decades owing to their serious toxic effects on nontarget organisms when leached into environment even at very low concentrations ($ng \cdot L^{-1}$) [37]. Besides the fact that they are considered as endocrine disruptors among organometallic compounds, they also possess teratogenic properties and can cause disruption to the reproductive function in mammals, as well as could act as hepatoxins, immunotoxins, neurotoxins, and obesogens [35, 38].

In the following sections of this chapter, we will present quantitative and qualitative data about the presence of these compounds in different environmental compartments and biota samples.

3. Organomercury, organotin, and organolead detection from complex environmental and biota samples: local case study

Considering the extensive use from past and their improper disposal, as well the lack of evaluation of possible contaminated sites (from past activities) made that even in our days many of such sites to still being used either for agriculture or for pasture. Without a proper evaluation of contaminants, such as mercury, lead, or tin distribution and speciation in soils, and without an assessment of their risks to animals and humans, exposure to such contaminants could be occurred nowadays. To assess such risks for environment, biota, and public health protection purposes, it is imperative to consider their speciation both in soils, water, and in biota plant.

3.1. Environmental and biota sampling for organomercury, organotin, and organolead monitoring

Soil, water, and vegetable samples were collected from Turda region, Cluj district from the northwestern part of Transylvania ($46^\circ 34'$ and $23^\circ 47'E$) including Turda town, nearest rural regions and industrial zones—banned chemical factory, Romania (see **Figure 1**). Soil, water,

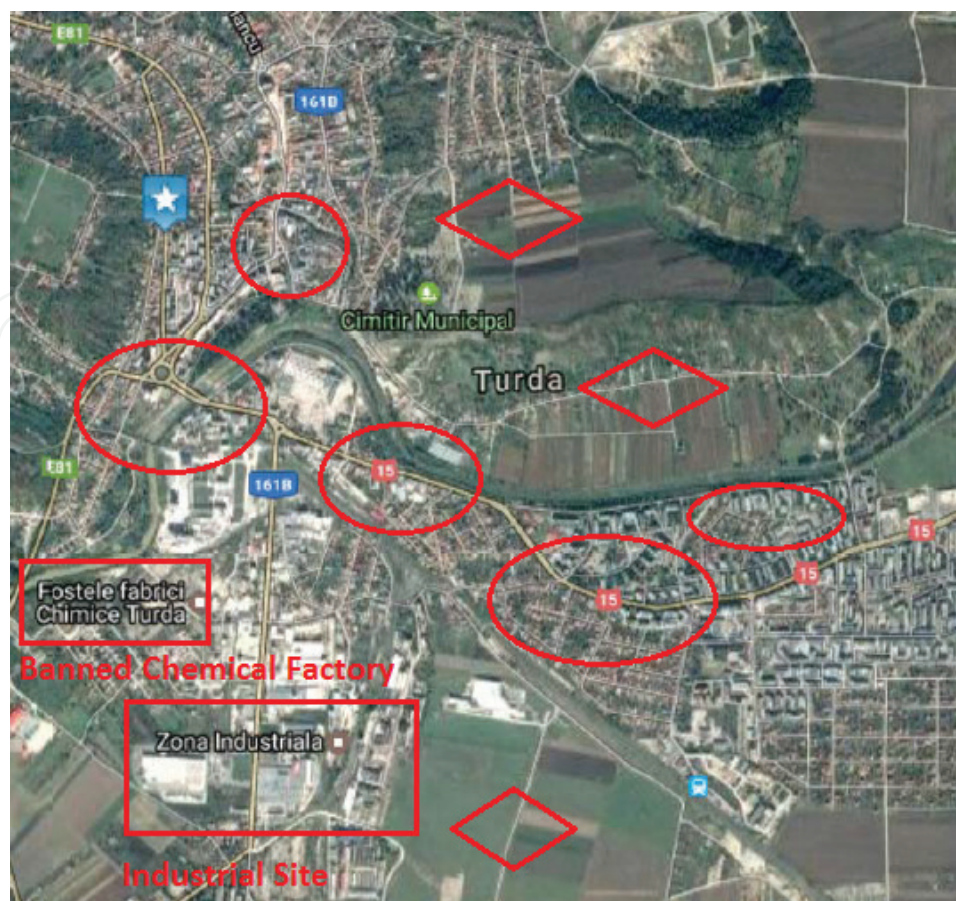


Figure 1. Sampling site map—rectangle corresponds to industrial sites; oval corresponds to inhabited areas; rhomb corresponds to agricultural sites.

and vegetable samples were collected in a period of March, July, and October for 2 years consecutively. Vegetables included for study were selected based on their edible part contact with different environmental compartments: leafy vegetables (lettuce, spinach, and cabbage), “root” and “bulb” vegetables (carrot, parsnip, onion, and garlic), and fruit vegetables (peas, tomato, and eggplant).

Soil and vegetable sample were collected with metallic collectors, returned to the laboratory in polyethylene bags and stored at -20°C . Before analysis, the samples were spread and dried at ambient temperature, and after drying samples were homogenized and shifted through a 2-mm stainless steel sieve.

Surface and well water were collected in polyethylene bottles excepting the cases when organic mercury species were the target analytes, the case when the samples were collected in Teflon containers in order to avoid metallic compound reaction with the bottle surface. Before all sampling campaign, the sampling bottles were subjected to acid cleaning with HNO_3 in order to remove possible metal impurities from the bottle’s wall and to prevent further metal adsorption [39]. All water samples were stored in dark at 4°C until analysis and analyzed in less than 7 days from sampling time.

3.2. Organomercury compounds analysis from soil, water, and vegetable samples

As previous work had shown that the organic species of mercury that were found to be important from hazard and toxicological point of view and those are prevalent in the environment are as follows methylmercury (CH_3Hg^+), ethylmercury ($\text{C}_2\text{H}_5\text{Hg}^+$) [23, 24], phenylmercury ($\text{C}_6\text{H}_5\text{Hg}^+$) [25], and dimethylmercury ($(\text{CH}_3)_2\text{Hg}$) [26].

3.2.1. Water analysis

According to Cai et al. [40] and with minor modifications, extraction and derivatization of organic forms of mercury were conducted using 20 mL of water sample that was placed in 40 mL amber glass vials sealed with screw caps with polytetrafluoroethylene (PTFE)-coated silicon rubber septum. Noted that 2 g of NaCl with 150 μL of 0.4% NaBEt_2 was added to the sample and the pH was set to 4.5 using acid acetic, and then the vials were immediately closed tightly. The derivatization step was acquired during 15 min at 70°C .

Afterward, a 50 μm /30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber was exposed to the solution headspace for 20 min, maintaining the same temperature (40°C) and assuring a continuous agitation with a rate of 175 rpm. Finally, the fiber was introduced in the chromatographic injector and the target compounds were thermally desorbed at 260°C for 5 min.

3.2.2. Soil and vegetal sample analysis

According to the method presented by Korbas et al. [41], 5 g of homogenized soil and their respective dried vegetable samples were put in an extraction tube with 1 mL of aqueous H_2SO_4 (14 M, saturated with cupric sulfate), 1 mL of 4 M KBr solution, and 20 mL of toluene. The mixture with samples was shaken for 30 min after that subjected to centrifugation for 15 min at 2000 rpm. The procedure was repeated once under the same condition, after that the collected supernatant organic phases were combined and back extracted with 20 mL of L-cysteine solution (1.5% w/v). The organic phase was separated once again after shaking and centrifugation process (2000 rpm for 15 min). From the obtained organic layer, water was removed using anhydrous Na_2SO_4 and from that 1 μL was injected into gas chromatograph inlet.

3.2.3. Gas chromatography-mass spectrometric analysis

Gas chromatography-mass spectrometric analysis was carried out on a GC Focus DSQ II equipment (Thermo Finnigan) using a TR-5MS capillary column with the following characteristics: 30 m \times 0.32 mm i.d., with a 0.25- μm film thickness. The mass spectrometer was operated in an electron impact ionization mode at 70 eV ionizing energy. The GC injection port temperature was set at 280°C while the detector source temperature was set at 250°C . Splitless mode was used for injection of 1 μL volume of extracts. Applied temperature program for column oven started from 80°C (3 min) to $150^\circ\text{C}\cdot\text{min}^{-1}$ with a rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ and maintained at 150°C for 5 min followed by an increase of $10^\circ\text{C}\cdot\text{min}^{-1}$ until 280°C and maintained at this final temperature for 5 min. Identification of the target compounds was done through full scan monitoring mode ranging between 50 and 600 m/z.

3.3. Organolead compounds analysis from soil, water, and vegetable samples

Organolead compounds are found in major environmental compartments not only as a consequence of their use in anthropogenic activity, but also via naturally as a consequence of biomethylation processes. As mentioned earlier, the toxicity of these groups of compounds was widely demonstrated, it is known that tetraethyllead (TEL) is much more toxic to animals [16] while ionic alkyllead compound was found to be more toxic to plants [42], with both showing higher toxicity than inorganic lead, mainly due to their liposolubility [43]. Generally, it is accepted that the toxicity of organolead compounds increases with the degree of alkylation, respecting the following sequence tetraethyllead > triethyllead > diethyllead > monoethyllead [30].

Target organolead compounds of this study were tetraethyllead (TEL), followed by its transformation products in environment, as triethyllead (TREL), diethyllead (DEL), and monoethyllead (MEL) resulted from dealkylation reactions having as standard their chlorinated forms.

3.3.1. Water analysis

The extraction and derivatization of organic forms of lead is similar to the extraction of organotin species. Shortly, 10 mL of water sample was placed in 40 mL amber glass vials sealed with screw caps with PTFE-coated silicon rubber septum. Noted that 2 g of NaCl with 500 μ L of 0.4% NaBEt₂ was added to sample and the pH was set at 4.5 using acid acetic, after that the vials were immediately tightly closed. The derivatization step was acquired during 100 min at 40°C.

Afterward, 100- μ m polydimethylsiloxane (PDMS) fiber was exposed to the solution headspace for 20 min, maintaining the same temperature (40°C) and ensuring a continuous agitation with a rate of 175 rpm. Finally, the fiber was introduced in the chromatographic injector and the target compounds were thermally desorbed at 260°C for 5 min.

3.3.2. Soil and vegetable sample analysis

The extraction of organolead compounds from soil and vegetable samples was acquired ultrasound assisted for 20 min using 10 g of samples and 50 mL of n-hexane. The supernatant was collected and the extraction was repeated once again under the same conditions. Collected supernatants were rotary evaporated until 1 mL. The concentrate was mixed with 300 μ L of NaBEt₄ (2 g NaBEt₄ in 10 mL ethanol), used as a derivatization agent for detection and quantification of the target organic lead compounds. The obtained extract mix was subjected to gas chromatography-mass spectrometric (GC-MS) analysis.

3.3.3. Gas chromatography-mass spectrometric analysis

This was carried out on a GC Focus DSQ II equipment (Thermo Finnigan) using a TR-5MS capillary column with the following characteristics: 30 m \times 0.25 mm i.d. with a 0.25- μ m film thickness. The mass spectrometer was operated in an electron impact ionization mode at 70 eV ionizing energy. The GC injector was set at 260°C while the detector source temperature was set at 280°C. Splitless mode was used for injection of 1 μ L volume of extracts. Applied temperature program for column oven was started from 50°C (5 min) to 100°C·min⁻¹ with a

rate of $7^{\circ}\text{C}\cdot\text{min}^{-1}$ and maintained at 100°C for 2 min followed then by an increase of $15^{\circ}\text{C}\cdot\text{min}^{-1}$ until 280°C and maintained at this final temperature for 10 min also. The identification of target compounds was done through a full-scan monitoring mode between the range of 50 and 600 m/z .

3.4. Organotin compounds analysis from soil, water, and vegetable samples

In this work, a field study was conducted investigating the pathways of organotins in soil-water environment and their uptake potential in vegetables grown on possible contaminated areas.

Monitored organotin compounds were as follows: monobutyltin trichloride (MBT), monophenyltin trichloride (MPT), diphenyltin dichloride (DPT), dibutyltin dichloride (DBT), tributyltin chloride (TBT), and triphenyltin chloride (TPT).

3.4.1. Water samples analysis

Water samples preparation for analysis were done as presented by Kovacs et al. [39] and Hu et al. [44] with minor modifications as follows: about 20 mL of water sample was placed in 40 mL amber glass vials sealed with screw caps with PTFE-coated silicon rubber septum. Noted that 1.5 g of NaCl, 2 mL of acetate buffer (acetate buffer: $82\text{ g}\cdot\text{L}^{-1}$ sodium acetate in water adjusted to pH 5 with acetic acid), and 100 μL of NaBEt_4 solution (2 g NaBEt_4 in 10 mL ethanol) had been added to water sample and the vials were immediately closed and stirred on a magnetic stirrer at 100 rpm and 20°C . The optimal SPME fiber for organotin compounds extraction was found to be 100 μm polydimethylsiloxane (PDMS)-coated fiber. SPME was performed in the headspace. Use of NaBEt_4 solution allowed the organotin compounds to be derivatized *in-situ* and simultaneously extracted into the PDMS phase. The fiber was exposed to the headspace for 30 min under continuous stirring, after that the fiber was withdrawn into the needle of the holder and the SPME was placed into the GC injector at 240°C for 10 min in order to allow target compound desorption.

3.4.2. Soil and vegetal sample analysis

The extraction of organotin compounds from soil and vegetable samples was done according to the method presented by Hu et al. [44] with minor modifications as follows: 5 g of soil and vegetables, respectively, were extracted with 50 mL methanol that contains 2 mL of hydrochloric acid (37%) by ultrasonic shaking at 50°C for 30 min. The extraction was repeated twice with 30 mL methanol containing 1.2 mL hydrochloric acid (37%). The supernatants were combined and transferred to a separation funnel containing 100 mL of 30% (w/v) sodium chloride salt and 50 mL of dichloromethane and shaken manually for 10 min. The extraction procedure was repeated in the same manner, after that the collected organic layers were united and subjected for concentration through a rotary evaporator almost until to dryness. The concentrate was mixed with a pH 5.0 buffer solution (acetate buffer: $82\text{ g}\cdot\text{L}^{-1}$ sodium acetate in water adjusted to pH 5 with acetic acid) and 120 μL of NaBEt_4 (2 g NaBEt_4 in 10 mL ethanol) was used as a derivatization agent for the target organic tin compounds detection and quantification. The

ethylated organotin compounds were extracted with 5 mL of hexane three times after that the extracts were cleaned up using florisil column. The collected organic fraction was concentrated at 1 mL after that the obtained extracts were subjected to gas chromatography-mass spectrometric (GC-MS) analysis.

3.4.3. Gas chromatography-mass spectrometric analysis

It was carried out on a GC Focus DSQ II equipment (Thermo Finnigan) using a TR-5MS capillary column with the following characteristics: 60 m × 0.25 mm i.d. with a 0.25-μm film thickness. The mass spectrometer was operated in an electron impact ionization mode at 70 eV ionizing energy. The GC injector was set at 270°C while the detector source temperature was set at 280°C. Splitless mode was used for injection of 1 μL volume of extracts. Applied temperature program for column oven was started from 50°C (5 min) to 130°C·min⁻¹ with a rate of 15°C·min⁻¹ and maintained at 130°C for 10 min followed then by an increase of 15°C·min⁻¹ until 280°C and maintained at this final temperature for 10 min.

Identification of target compounds was done through a selective ion-monitoring mode, and the fragment ions were those most abundant in each oligomers. Their values are presented in **Table 1**.

Ions monitored in SIM mode for organotin compounds		
Organotin compounds	Primary characteristic ion* (m/z)	Secondary ions (m/z)
MBT	149	179, 233, 235
DBT	149	179, 207, 263
TBT	149	177, 207, 263
MPT	195	253, 255
DPT	275	301, 303
TPT	197	349, 351

*Quantitation ion.

Table 1. Monitored ions in selective ion monitoring mode (SIM) of target organometallic compounds.

4. Organomercury, organotin, and organolead and their “fingerprint” on environmental compartments and surrounding biota: case study, Turda region

The presence of these organometallic compounds surrounding us has raised a great deal of concern in the past few decades because of their high toxicity to nontarget organisms when leached into different environmental compartments, even at low concentrations [2, 23, 33]. At these moments, most studies regarding organometallic compounds present in the environment were conducted on aquatic environment. Studies considering soil or air contamination with

organometallic compounds were most of the time conducted on industrial sites and mining areas. Similarly, although studies on bioconcentration and biomagnification of organometallic compounds were done on a large scale of species from the aquatic environment, according to our knowledge, there is minor information in the literature considering organometallic compounds uptake potential by vegetables.

In this work, a field study was conducted investigating the pathways of organometallic compounds (tin, lead, and mercury species) in soil-water environment and their uptake potential in vegetables grown on inhabited area—Turda region, including rural, urban, and agricultural sites considering these sites as possible contaminated areas due to the presence of an old chemical production plant (chemicals factory Turda) which was closed from more than 20 years.

4.1. Organic compounds analysis in environmental samples: case study, Turda region—Cluj, Romania

Surface water as well as underground water samples were collected from the mentioned sites (rural, urban, agricultural, and industrial areas) in order to evaluate if there are any signs considering the potential of past pollution. Considering surface water samples, total 22 sampling points were selected for surface water status evaluation. Specifically, 7 sampling points were selected located on the banned industrial sites, 10 sampling points from inhabited areas (3 sampling points from Turda town and 7 sampling points from rural areas), and 5 sampling points from the agricultural place. Wells water, totally from 21 sampling sites, were collected as follows: 3 sampling points were selected located on the banned industrial sites, 14 sampling points from inhabited areas (4 sampling points from Turda town and 10 sampling points from rural areas), and 4 sampling points from agricultural place.

Organometallic compounds detected in water samples including surface and well water (underground water) showed higher levels in the samples collected from old industrial site than in the other sampling locations (inhabited area—rural and urban, and agricultural sites). The range of organotin, organolead, and organomercury amount detected in the water samples vary between 0.1 and 72, 0.2 and 15.9, and 0.08 and 61.4 $\mu\text{g}\cdot\text{L}^{-1}$, respectively.

Considering **Figure 2**, it could be observed that the organometallic compounds that were detected in the higher amount in the samples collected from the banned industrial area were methylmercury, ethylmercury, tetraethyllead, and triphenyltin with the average amounts of 26.8, 11.4, 19.5, and 37.7 $\mu\text{g}\cdot\text{L}^{-1}$, respectively.

Excluding amount value of water samples collected from the banned industrial area, higher values, with 15–20%, of monitored organometallic compounds were observed in the case of underground water samples than those of surface water samples.

Compounds, such as dimethylmercury, monoethyllead, monobutyltin, monophenyltin, and diphenyltin were detected just in 41% in the collected water samples. This could be attributed to their instability considering their physicochemical properties. Taking into account the variations between the period of sampling (March, July, and October), no significant differences were observed.

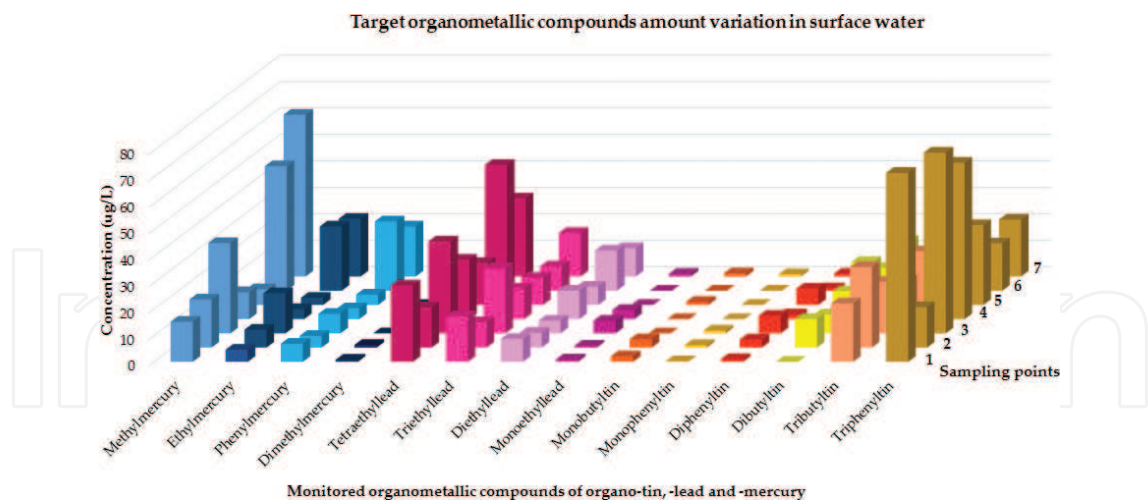


Figure 2. Target organometallic compounds amount ($\mu\text{g}\cdot\text{L}^{-1}$) in surface water sampling points from industrial sites

Analysis of soil samples, totally 29 (inhabited areas: 7 sampling points from Turda town and 14 sampling points from villages; 5 from agricultural areas; and 3 from banned industrial sites) has shown higher amounts than analysis from water samples. Soil samples were collected from horizon 0, and from 15 and 30 cm depth, respectively. Between the layers, minor decreasing tendency was observed once with decreasing the depth.

Comparing detected amounts of organomercury compounds of soil samples from a rural area with those of wells water from the same region (Figure 3), it was observed that the average value of all four monitored organomercury compounds were approximately twofold higher in the case of soil samples than in well water (underground water).

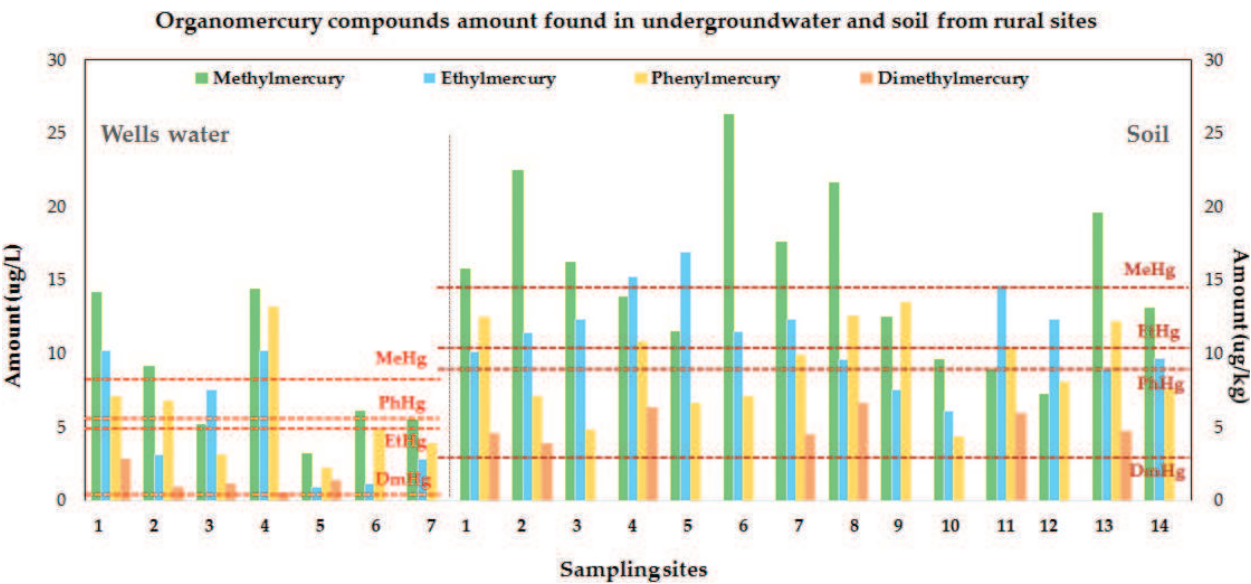


Figure 3. Organomercury compound variation in underground water (wells) and soil from rural sites.

Organotin compounds were detected at a higher percentage in samples from the industrial area compared to the rest of sampling locations (urban, rural, or agricultural areas). Monobutyltin and monophenyl tin were detected just in 40% of the collected samples—including water and soil samples from all sampling sites. This could be caused by their weak stability in the environment.

According to **Figure 4**, the average values of organotin compounds increase once with increasing their degree of alkylation in both the case of water as well as soil samples. In soil samples collected on depth layers, in most cases the organotin compounds were extremely lower in the surface horizons and the amount starts to increase once with depth (see **Figure 4**).

The total amount of organotin compounds in water and soil samples collected from the banned industrial site vary between 38 and 364.1 ppm while from the rest of sampling location the total amount of organotin compounds vary between 3.4 and 21.5, 1.6 and 31.5, and 1.4 and 28.9 ppm.

With regard to organolead compounds, no correlation was found between the detected amounts and sampling locations, as shown in **Table 2**.

4.2. Organometallic compounds uptake by vegetables grown on possible contaminated sites: case study, Turda region—Cluj, Romania

The major pathway of living organism's exposure to contaminants in soil is through food ingestion (food web). The prediction or estimation of risks to living organisms requires knowledge about both environmental contamination and food contamination. The direct measurement of contaminant concentration in living organisms' food is advisable to minimize uncertainty in ecological risk assessment [45]. However, site-specific data on the bioaccumulation of contaminants in vegetation and other biota that comprise living organisms diet are often not available because of constraints in funding and/or time, most of the analysis being expensive and time-consuming.

Most time, the concentration of chemical contaminants is measured at the known contaminated sites prior to a risk assessment. The challenge for the development of numerical models that are able to estimate the concentration of contaminants accumulated in plants (as vegetables, crops, etc.) is the soil-plant uptake factor. Soil-plant uptake factor refers to the ratio of a contaminant in plants to that in soil. The concentration of a contaminant in plant at a particular location is estimated by multiplying the measured concentration in soil by the soil-plant uptake factor [45].

Usually, the concentrations of monitored contaminant in mature plants and soil are assumed to be at equilibrium, thus exposure time is not necessary to be considered. However, in nature the bioavailability of organometallic compounds depend on the geochemical nature, pedoclimatic variables (temperature and rain intensity) and related to fluctuations of physicochemistry of the medium, such as soil moisture, pH, and soil organic matter content [46]. On the other side, the bio-uptake process depends on the internalization pathways of plant species which refer to the ability of organometallic compounds to cross the biological barrier. That, most of the time, is determined by the concentration of flux of internalized organometallic compounds but studied has showed that this ability of plants depends also on their size, nature, and physiology.

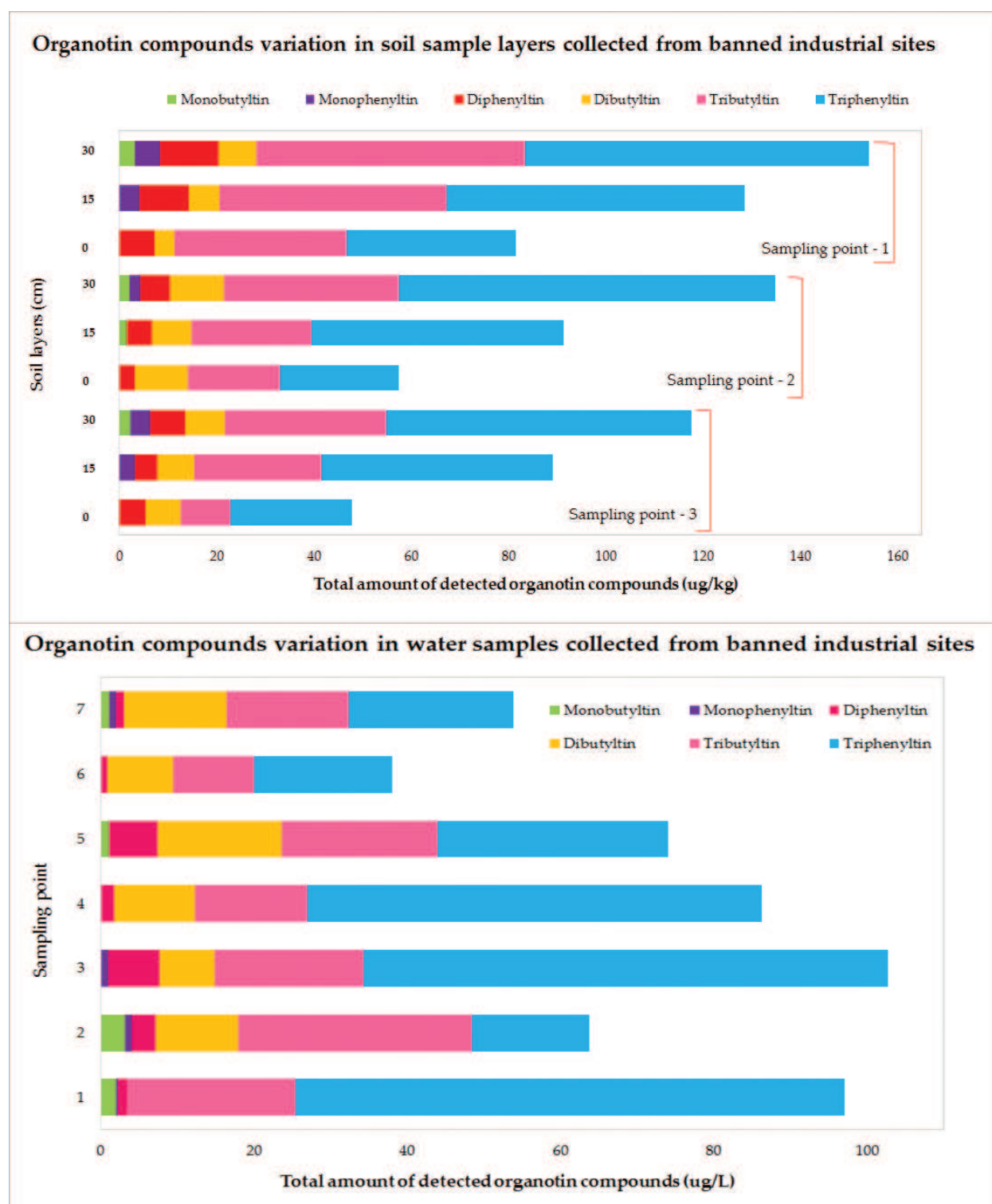


Figure 4. Organotin compound variation between soil (layers) and water samples collected from the sampling points of banned industrial sites.

The uptake factor of monitored organometallic compounds varied between plants (considering their edible part contact with contaminated environmental matrix), see **Table 3**. With respect to their fates in relationship to plant uptake, organometallic compounds in soil can be roughly divided into three groups according to their uptake factors: lowest average uptake

Organolead compounds			TEL			TREL			DEL			MEL		
Sample type No.			Range	Average	N.S.U.D.	Range	Average	N.S.U.D.	Range	Average	N.S.U.D.	Range	Average	N.S.U.D.
Banned industrial site	Soil ($\mu\text{g}\cdot\text{kg}^{-1}$)	3	0.1–34.2	12.8	–	0.5–21.5	8.6	–	0.4–7.2	3.8	1	0.5–4.9	0.8	1
	Surface water ($\mu\text{g}\cdot\text{L}^{-1}$)	7	0.2–18.5	5.9	3	0.3–15.5	6.7	2	0.4–10.8	3.9	2	0.4–5.1	1.2	4
	Well waters ($\mu\text{g}\cdot\text{L}^{-1}$)	3	0.2–25.8	11.5	1	0.4–18.2	7.1	–	0.3–6.9	2.4	1	0.5–3.8	0.9	2
Urban site	Soil ($\mu\text{g}\cdot\text{kg}^{-1}$)	7	0.5–10.2	3.5	2	1.2–13.5	6.5	1	0.5–11.8	3.2	2	1.5–5.9	1.8	2
	Surface water ($\mu\text{g}\cdot\text{L}^{-1}$)	3	0.2–8.7	2.9	–	0.8–9.2	2.8	–	0.2–5.9	1.8	1	0.4–3.5	0.7	1
	Well waters ($\mu\text{g}\cdot\text{L}^{-1}$)	4	0.4–12.6	4.5	–	0.4–5.5	3.1	–	0.4–9.7	2.3	1	0.2–4.9	2.5	1
Rural site	Soil ($\mu\text{g}\cdot\text{kg}^{-1}$)	14	0.3–21.8	10.5	3	0.5–16.2	5.8	2	0.2–7.4	3.8	4	1.2–6.2	2.6	6
	Surface water ($\mu\text{g}\cdot\text{L}^{-1}$)	7	1.2–15.5	5.5	2	0.2–6.7	2.1	1	0.4–4.2	1.5	2	0.4–3.9	0.8	3
	Well waters ($\mu\text{g}\cdot\text{L}^{-1}$)	10	2.8–16.7	8.2	4	0.4–15.5	3.9	3	0.4–6.1	3.1	2	0. –6.2	3.5	4

Organolead compounds			TEL			TREL			DEL			MEL		
Sample type No.			Range	Average	N.S.U.D.	Range	Average	N.S.U.D.	Range	Average	N.S.U.D.	Range	Average	N.S.U.D.
Agricultural site	Soil ($\mu\text{g}\cdot\text{kg}^{-1}$)	5	1.5–20.4	7.7	–	0.1–13.2	7.5	1	0.2–13.5	5.2	2	0.5–4.8	1.6	2
	Surface water ($\mu\text{g}\cdot\text{L}^{-1}$)	5	0.5–13.2	3.5	–	0.2–6.8	1.8	1	0.4–7.9	3.8	1	0.3–2.8	1.1	2
	Well waters ($\mu\text{g}\cdot\text{L}^{-1}$)	4	0.2–13.5	8.5	–	0.2–9.5	4.2	–	1.2–5.8	2.1	–	0.2–3.7	0.9	1

Notes: TEL, tetraethyllead; TREL, triethyllead; DEL, diethyllead; MEL, monoethyllead; No, –number of sample collected; N.S.U.D, number of samples in which the target compounds was not detected.

Table 2. Organolead species variation between sampling sites.

Organometallic compounds	Leafy vegetables (<i>n</i> = 102)		Root and bulb vegetables (<i>n</i> = 115)		Fruit vegetables (<i>n</i> = 95)	
	Average	Min/Max.	Average	Min/Max.	Average	Min/Max.
Methylmercury	0.64	0.02–1.05	0.84	0.07–1.57	0.57	0.02–1.81
Ethylmercury	0.74	0.04–1.84	0.94	0.04–1.84	0.61	0.004–1.37
Phenylmercury	0.48	0.007–1.15	1.14	0.008–1.61	0.24	0.005–0.98
Dimethylmercury	0.44	0.08–1.24	1.06	0.004–1.28	0.15	0.02–0.87
Tetraethyllead	1.24	0.004–1.51	1.15	0.08–1.47	0.44	0.002–0.98
Triethyllead	1.05	0.002–1.61	0.95	0.003–1.27	0.51	0.01–1.05
Diethyllead	0.42	0.05–0.98	0.61	0.005–1.36	0.38	0.002–0.74
Monoethyllead	0.34	0.04–0.54	0.27	0.05–0.84	0.18	0.002–0.44
Monobutyltin	0.28	0.006–0.49	0.19	0.001–0.31	0.17	0.001–0.39
Monophenyltin	0.18	0.002–0.37	0.11	0.002–0.41	0.24	0.002–0.58
Diphenyltin	0.46	0.001–0.49	0.24	0.005–0.64	0.33	0.01–0.77
Dibutyltin	0.22	0.005–0.57	0.41	0.001–0.81	0.19	0.002–0.69
Tributyltin	1.24	0.002–1.65	0.67	0.004–0.79	0.47	0.02–1.09
Triphenyltin	1.09	0.05–1.74	0.53	0.002–1.15	0.61	0.008–1.11

n = number of vegetable samples.

Table 3. Uptake factors range for monitored organometallic compounds.

factor (between 0.001 and 0.05), medium average uptake factor (0.05–0.1), and highest average uptake factor (0.1–1). The highest uptake factors for almost all monitored organometallic compounds were determined in the case of root and bulb vegetables, followed by leafy vegetables, and finally by fruit vegetables (see **Table 3**).

Lowest uptake factors were determined in the case of monoethyllead, monobutyltin, monophenyltin, diphenyltin, and dibutyltin regardless of plant species group (leafy, root, bulb, fruit, and vegetables).

5. Summary

The problem of trace metals pollution is transformation of the original pollutants into other species as organometallic compounds of mercury, tin, and lead species that are considered frequently more toxic and mobile in the environment than their corresponding parent compound. Although organometallic compounds occurrence in the environment could be natural, most of the time their quantitative presence is associated with anthropogenic sources and activities. Organometallic amounts in detected environmental samples increased once with their degree of alkylation in the case of all three groups studied (tin, lead, and mercury).

Based on the literature data, worldwide observations showed that a clear relation is observed between organometallic compound concentrations in the soils/underground water and the accumulation of this element in plants. In the case of monitored organometallic compounds, the higher amounts were detected in root and bulb vegetables followed by leafy, vegetables, and fruit vegetables. The uptake factor increased once with the degree of alkylation in the case of all groups studied.

Author details

Kovacs Melinda Haydee^{1*} and Kovacs Emoke Dalma^{1,2}

*Address all correspondence to: haydee.kovacs.melinda@gmail.com

1 Research Institute for Analytical Instrumentation, INCDO-INOE 2000, Cluj-Napoca, Romania

2 Chemistry and Chemical Engineering Faculty, Babes-Bolyai University, Cluj-Napoca, Romania

References

- [1] Ding Q, Cheng G, Wang Y, Zhuang D. Effects of natural factors on the spatial distribution of heavy metals in soils surrounding mining regions. *Science of the Total Environment*. 2017;**578**:577-585

- [2] Lee R, Oshima Y. Effects of selected pesticides, metals and organometallics on development of blue crab (*Callinectes sapidus*) embryos. *Marine Environmental Research*. 1998;**46**(1-5):479-482
- [3] Office of the Science Advisor – Risk Assessment Forum, editor. Framework for Metal Risk Assessment. Washington DC, USA: U.S. Environmental Protection Agency; 2007. p. 172. DOI: EPA 120/R-07/001
- [4] Wu SH, Shi YX, Zhou SL, Wang CH, Chen H. Modelling and mapping of critical loads for heavy metals in Kunshan soil. *Science of the Total Environment*. 2016;**569-570**:191-200
- [5] Henriques B, Rodrigues SM, Coelho C, Cruz N, Duarte AC, Romkens PFAM, Pereira E. Risks associated with the transfer of toxic organo-metallic mercury from soils into the terrestrial feed chain. *Environmental International*. 2013;**59**:408-417
- [6] Hu H, Li Z, Feng Y, Liu Y, Xue J, Davis M, Liang Y. Prediction model for mercury transfer from soil to corn grain and its cross-species extrapolation. *Journal of Integrative Agriculture*. 2016;**15**(10):2393-2402
- [7] Pan LB, Ma J, Wang XL, Hou H. Heavy metals in soils from a typical county in Shanxi Province, China: Levels, sources and spatial distribution. *Chemosphere*. 2016;**148**:248-254
- [8] Aran D, Gury M, Jeanroy E. Organo-metallic complexes in an Andosol: A comparative study with a Cambisol and Podzol. *Geoderma*. 2001;**97**(1-2):65-79
- [9] Lu M, Wu XJ, Zheng DC, Liao Y. Distribution of PCDD/Fs and organometallic compounds in sewage sludge of wastewater treatment plants in China. *Environmental Pollution*. 2012;**171**:78-84
- [10] Zhaou YJ, He JC, Chen Q, He J, Hou HQ, Zheng Z. Evaluation of 206 nm UV radiation transformation for degrading organometallics in wastewater. *Chemical Engineering Journal*. 2011;**167**(1):22-27
- [11] Reis AT, Rodrigues SM, Davidson CM, Pereira E, Duarte AC. Extractability and mobility of mercury from agricultural soils surrounding industrial and mining contaminated areas. *Chemosphere*. 2010;**81**(11):1369-1377
- [12] Biester H, Muller G, Scholer HF. Binding and mobility of mercury in soils contaminated by emissions from chloralkali plants. *Science of the Total Environment*. 2002;**284**:191-203
- [13] Selin N.E. Global biogeochemical cycling of mercury: A review. *Annual Review of Environment and Resources*. 2009;**34**:43-63
- [14] Challa YR, Astudillo LRD, Ramirez A, Escalona A, Martinez G. Distribution of total and organic mercury in superficial soils in the upon Manzanares River watershed, Sucre State, Venezuela. *Air, Soil and Water Research*. 2008;**1**:21-29
- [15] Clarkson TW, Magos L. The toxicology of mercury and its chemical components. *Critical Review in Toxicology*. 2006;**36**:609-662

- [16] Craig PJ, Eng G, Jenkins RO. Occurrence and pathways of organometallic compounds in the environment – general considerations. In: Craig PJ, editor. *Organometallic Compounds Occurrence in the Environment*. 2nd ed. England: John Wiley & Sons Ltd; 2003. pp. 1-56
- [17] Briant N, Chouvelon T, Martinez L, Brach-Papa C, Chiffolleau JF, Savoye N, Sonke J, Knoery J. Spatial and temporal distribution of mercury and methylmercury in bivalves from the French coastline. *Marine Pollution Bulletin*. 2017;**114**(2):1096-1102
- [18] Chen L, Liu M, Fan R, Ma S, Xu Z, Ren M, He Q. Mercury speciation and emission from municipal solid waste incinerators in the Pearl River Delta, South China. *Science of the Total Environment*. 2013;**447**:396-402
- [19] Caballero B, Olguin N, Campos F, Farina M, Ballester F, Lopez-Espinosa MJ, et al. Methylmercury-induced developmental toxicity is associated with oxidative stress and cofilin phosphorylation. Cellular and human studies. *NeuroToxicology*. 2017;**59**:197-209. DOI: <http://dx.doi.org/10.1016/j.neuro.2016.05.018>
- [20] Ser PH, Omi S, Shimizu-Furusawa H, Yasutake A, Sakamoto M, Hachiya N, et al. Differences in the responses of three plasma selenium-containing proteins in relation to methylmercury-exposure through consumption of fish/whales. *Toxicology Letters*. 2017;**267**:53-58
- [21] Morita M, Yoshinaga J, Edmonds JS. The determination of mercury species in environment and biological samples (Technical Report). In: *Analytical Chemistry Division - Commission of Microchemical Techniques and Trace Analysis Working Group on Speciation*, editors. *Pure and Applied Chemistry*. 1st ed. Great Britain: IUPAC; 1998. pp. 1585-1615
- [22] Lindqvist O, Jernelov A, Johansson K, Rodhe H. Mercury in the Swedish environment: Global and local sources. In: *Report of the Workshop; November 1983; Lerum, Sweden*. Solna, Sweden: SNV PM I Swedish Environmental Protection Board; 1984. pp. 105-110
- [23] Marques RC, Abreu L, Bernardi JVE, Dorea JG. Neurodevelopment of Amazonian children exposed to ethylmercury (from Thimerosal in vaccines) and methylmercury (from fish). *Environmental Research*. 2016;**149**:259-265
- [24] Zimmermann LT, Santos DB, Naime AA, Leal RB, Dorea JG, Barbosa Jr F, et al. Comparative study on methyl- and ethylmercury-induced toxicity in C6 glioma cells and the potential role of LAT-1 in mediating mercurial-thiol complexes uptake. *NeuroToxicology*. 2013;**38**:1-8
- [25] Lee CH, Lin RH, Liu SH, Lin-Shiau SY. Distinct genotoxicity of phenylmercury acetate in human lymphocytes as compared with other mercury compounds. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*. 1997;**392**(3):269-276
- [26] Siegler WR, Nierenberg DW, Hickey WF. Fatal poisoning from liquid dimethylmercury: A neuropathologic study. *Human Pathology*. 1999;**30**(6):720-723

- [27] Zuniga MC, Jover E, Arancibia V, Bayona JM. Development of a methodology for the simultaneous determination of inorganic and organolead compounds using supercritical fluid extraction followed by gas chromatography-mass spectrometry and its application to environmental matrices. *Talanta*. 2009;**80**(2):504-510
- [28] Elizabeth O'Brien/The Lead Group Inc. The Lead Education and Abatement Design Group Working to Eliminate Lead Poisoning Globally and to Protect the Environment from Lead in all its Uses: Past, Current and New Uses ABN 25 819 463 114 [Internet]. 2007. Available from: http://www.lead.org.au/fs/fst27_20070524.html [Accessed: January 10, 2017]
- [29] Asian Clean Fuels Association. Africa fuel quality update – progress & challenges. *Asian Clean Fuels Association (ACFA News)*. 2010;**8**(5):1-6
- [30] Gallert C, Winter J. Bioremediation of soil contaminated with alkyllead compounds. *Water Research*. 2002;**36**(12):3130-3140
- [31] Blakey DH, Bayley JM, Douglas GR. Induction of chromosomal aberrations in Chinese hamster ovary cells by triethyllead acetate. *Mutation Research/Genetic Toxicology*. 1992;**298**(1):1-7
- [32] Pyrzynska K. Organolead speciation in environmental samples: A review. *Microchimica Acta*. 1996;**122**(3):279-293
- [33] Gao JM, Wu L, Chen YP, Zhou B, Guo JS, Zhang K, Ouyang WJ. Spatiotemporal distribution and risk assessment of organotins in the surface water of the Three Gorges Reservoir Region, China. *Chemosphere*. 2017;**171**:405-414
- [34] Hoch M. Organotin compounds in the environment – An overview. *Applied Geochemistry*. 2001;**16**:719-743
- [35] Cole RF, Mills GA, Parker R, Bolam T, Birchenough A, Kroger S, Fones GR. Trends in the analysis and monitoring of organotins in the aquatic environment. *Trends in Environmental Analytical Chemistry*. 2015;**8**:1-11
- [36] Birchenough AC, Barnes N, Evans SM, Hinz H, Kronke I, Moss C. A review and assessment of tributyltin contamination in the North Sea, based on surveys of tributyltin tissue burdens and imposex/intersex in the four species of neogastropods. *Marine Pollution Bulletin*. 2002;**44**:534-543
- [37] Nakanishi. Endocrine disruption induced by organotin compounds; organotins function as a powerful agonist for nuclear receptors rather than an aromatase inhibitor. *The Journal of Toxicological Sciences*. 2008;**33**:269-276
- [38] Zuo Z, Chen S, Wu T, Zhang J, Su Y, Chen Y, Wang C. Tributyltin causes obesity and hepatic steatosis in male mice. *Environmental Toxicology*. 2011;**26**(1):79-85
- [39] Kovacs MH, Ristoiu D, Voica C, Ristoiu T. Optimization of organometallic compounds extraction from aqueous samples in order to improve their gas chromatography-mass spectrometry analysis performance. *Romanian Journal of Physics*. 2013;**58**(1-2):204-210

- [40] Cai Y, Monsalud S, Jaffe R, Jones RD. Gas chromatographic determination of organo-mercury following aqueous derivatization with sodium tetraethylborate and sodium tetraphenylborate: Comparative study of gas chromatography coupled with atomic fluorescence spectrometry, atomic emission spectrometry and mass spectrometry. *Journal of Chromatography A*. 2000;**876**(1-2):23-34
- [41] Korbas M, Blechinger SR, Krone PH, Pickering IJ, George GN. Localizing organo-mercury uptake and accumulation in zebrafish larvae at the tissue and cellular level. *Proceedings of the National Academy of Science of the United States of America*. 2008;**105**(34):12108-12112
- [42] Fallon RD. Accelerated rates of organolead transformation following nutrient enrichment of contaminated ground water. *Bulletin of Environmental Contamination and Toxicology*. 1994;**53**(4):603-609
- [43] Penalver R, Campillo N, Hernandez-Cordoba M. Comparison of two derivatization reagents for the simultaneous determination of organolead and organomanganese compounds using solid-phase microextraction followed by gas chromatography with atomic emission detection. *Talanta*. 2011;**87**:268-275
- [44] Hu JJ, Zhen H, Wan Y, Gao J, An W, An L, Jin F, Jin X. Trophic magnification of tri-phenyltin in a marine food web of Bohai Bay, North China: Comparison to tributyltin. *Environmental Science and Technology*. 2006;**40**(10):3142-3147
- [45] Office of Environmental Management, Bechtel Jacobs Company LLC, editors. Empirical models for the uptake of inorganic chemicals from soil by plants. 1st ed. Oak Ridge National Laboratory, USA: East Tennessee Technology Park; 1998. p. 116
- [46] Temmerman LD, Waegeneers N, Thiry C, Laing GD, Tack F, Ruttens A. Selenium content of Belgian cultivated soils and its uptake by field crops and vegetables. *Science of the Total Environment*. 2014;**468-469**:77-82

IntechOpen

